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A SPECIAL ARC PROCESS FOR NITROGEN FIXATION

By

Edgar DeBolt McCollum

A Thesis

Submitted for the Degree of

MASTER OF SCIENCE

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Since Priestly showed that oxygen and nitrogen unite through the aid of the electric arc, the conversion of atmospheric nitrogen into nitrates has been studied in a theoretical and a practical way by many investigators. That the commercial world is interested in the arc process is not surprising especially when one considers that the atmosphere contains the necessary raw materials, and that these raw materials will always be available. In spite of the fact that an enormous amount of work has been done on this subject, there still remain many possibilities in this field in an experimental and a theoretical way.

Theory

The oxidation of the nitrogen of the air is an equilibrium problem, the reaction taking place according to the following equation $N_2 + O_2 = 2NO$. Like all other reversible reactions the equilibrium is affected by temperature. There is very little union between nitrogen and oxygen at room temperature. At 2400° (absolute) 1.116% of an atmosphere of these two gases unite to form nitric oxide. Muthmann and Hofer were among the first to determine the equilibrium in the above reaction. (ber., 1903, 36,438). They found that the equilibrium constant increased with the temperature, a result which agrees well with the theory. Later Nernst investigated the equilibrium of nitric oxide, (Zeitsch Elektrochem., 1906, 12, 527) and found that the yield of nitric oxide increased with the temperature as shown in the following table.

Temp. Absolute	Concentration of nitric oxide	Investigator
1811	.37	Nernst
1877	.42	Jellinek
2023	.52	Jellinek
2033	.64	Nernst
2195	.97	Nernst
2580	2.05	Nernst
2675	2.23	Nernst

While the absolute temperature rises from 1811° to 2675° , an increase of 864° , the concentration increases from .37 to 2.23%. This is an increase of 500%.

Nernst's work appears to indicate that the percentage which does unite is a function of the temperature only. His work was done as follows. Dry air was passed through a ~~rubid~~ium vessel which was shaped like a pipette. The vessel was maintained at a constant temperature by means of an electrically heated furnace. The gases were led from the reaction chamber by means of a small cooled capillary. The cooled gas was then analyzed and the proportions of nitrogen, oxygen, and nitric oxide at equilibrium obtained. 43200 calories are required to form two moles of nitric oxide from the elements, then according to Vant Hoff's principle, an increase in temperature will cause the formation of nitric oxide, that is assuming that the above reaction is a purely thermal one.

It was thought at first that electrical action did not affect the yield of nitric oxide in the arc, and that the reaction was a thermal one. The arc was looked upon merely as a

source of high temperature. The results of Leblanc and Nuranen were in harmony with this belief. They found that the oxidation of nitrogen in the arc obeyed the law of mass action. Later Grau and Russ performed a series of experiments, and they concluded that the law of mass action holds in this case. The early investigators believed that if electrical action entered in, then the yield ought to be different for direct and alternating current. Lee and Beyer (*Zeitsch Elektrochem*, 1907, 13, 701) found that direct and alternating current under like conditions produced about equal yields. It has also been shown that frequency has very little influence on the reaction.

For a time it was accepted that the action in the arc was brought about only by high temperature. Among the first to point out that there might be an electrical influence, were Haber and Koenig. They called attention to the fact that nitric oxide is produced from its elements by the action of silent discharges at ordinary temperatures. The concentration of nitric oxide in thermal equilibrium at ordinary temperature is practically zero. They believed that in the arc the thermal equilibrium offset the electrical equilibrium, due to the fact that the high temperature decomposed the excess nitric oxide produced by the electrical action. Another argument in favor of the electrical theory is that Haber and Koenig obtained concentrations of nitric oxide which correspond to a temperature of 4700°C . Although they did not know the temperature of their arc, they thought that it was not above 3000°C at the highest, and that it might not have been above the melting point of

platinum. Furthermore according to the thermal theory the results with air and inverted air should be the same, as the following will show. $K = \frac{(\text{NO})^2}{(\text{N}_2)(\text{O}_2)}$ or $(\text{NO})^2 = K(\text{N}_2)(\text{O}_2)$. The concentration of nitric oxide should be the same when we have 80% nitrogen and 20% oxygen or 80% oxygen and 20% nitrogen. It has been found that the concentration of nitric oxide in the two cases differs beyond the limits of experimental error. The electrical equilibrium can be explained by considering that under the potential gradient between the electrodes, ions are formed by collisions and these ions lead to chemical formations and decompositions.

Another theory which has been brought forward in nitrogen oxidation is that nitrogen or oxygen or both are activated in the arc. It has been suggested that ozone was formed and that in decomposing the atomic oxygen oxidized the nitrogen.

Since nitrogen and oxygen are united by means of the silent discharge, it is possible that the oxidation of nitrogen is a photochemical reaction. Under the influence of the silent discharge ammonia is decomposed into hydrogen and nitrogen. Nitrogen and watervapor unite to form ammonium nitrite, and acetylene is polymerized. The best known of these reactions is that of ozone. Warburg showed that the ozone formation was not due to electrolysis produced by the current. He obtained a yield of ozone which corresponded to one thousand times the quantity of electricity sent through. It has been shown that chemically active ultra-violet rays are produced by the silent discharge in the gas. Perhaps the action of nitrogen and oxy-

gen in the silent discharge resembles that of ozone. The photochemical action might be catalytic like that of hydrogen and chlorine.?

There is no conclusive evidence that any one of these four theories is the correct one. It is hard to see how a thermodynamic calculation of the equilibrium in the arc means much. As said before concentrations of nitric oxide have been obtained in the arc which corresponds to a temperature of 4700°C . In an alternating current arc the temperature undoubtedly varies in all parts of the arc, so that a mean temperature means little. The problem of nitrogen fixation is one of rapid cooling no matter what theory is the correct one, because we have thermal decomposition. This can be brought about by removing the gases from the region of the arc as quickly as possible. The main difference in all arc processes consists chiefly in the means of producing the relative motion between the arc and air.

The effect of temperature on the dissociation of nitric oxide is shown by the following table. (Chem. Met. Eng. 22, 299-306).

Temp. Absolute	Dissociation time of nitric oxide to one-half value	
	Seconds	Hours
800		557
1000		39.7
1200	10200	2.83
1400	730	.203
1500	52.4	

Temp. Absolute Dissociation time of nitric oxide to
one-half value

	Seconds	Hours
1800	3.73	
2000	.266	
2200	.019	
2400	1360 micro-sec.	
2600	97.1	
2800	6.94	
3000	.493	
3200	.0353	
3400	2520 micro-sec.	
3600	180	
3800	12.9	
4000	.917	
4200	.0658	

At 1200° (absolute) 2.83 hours are required to decompose one-half of an atmosphere of nitric oxide. This shows that at a temperature of 1200° (absolute) or lower the decomposition of nitric oxide is negligible.

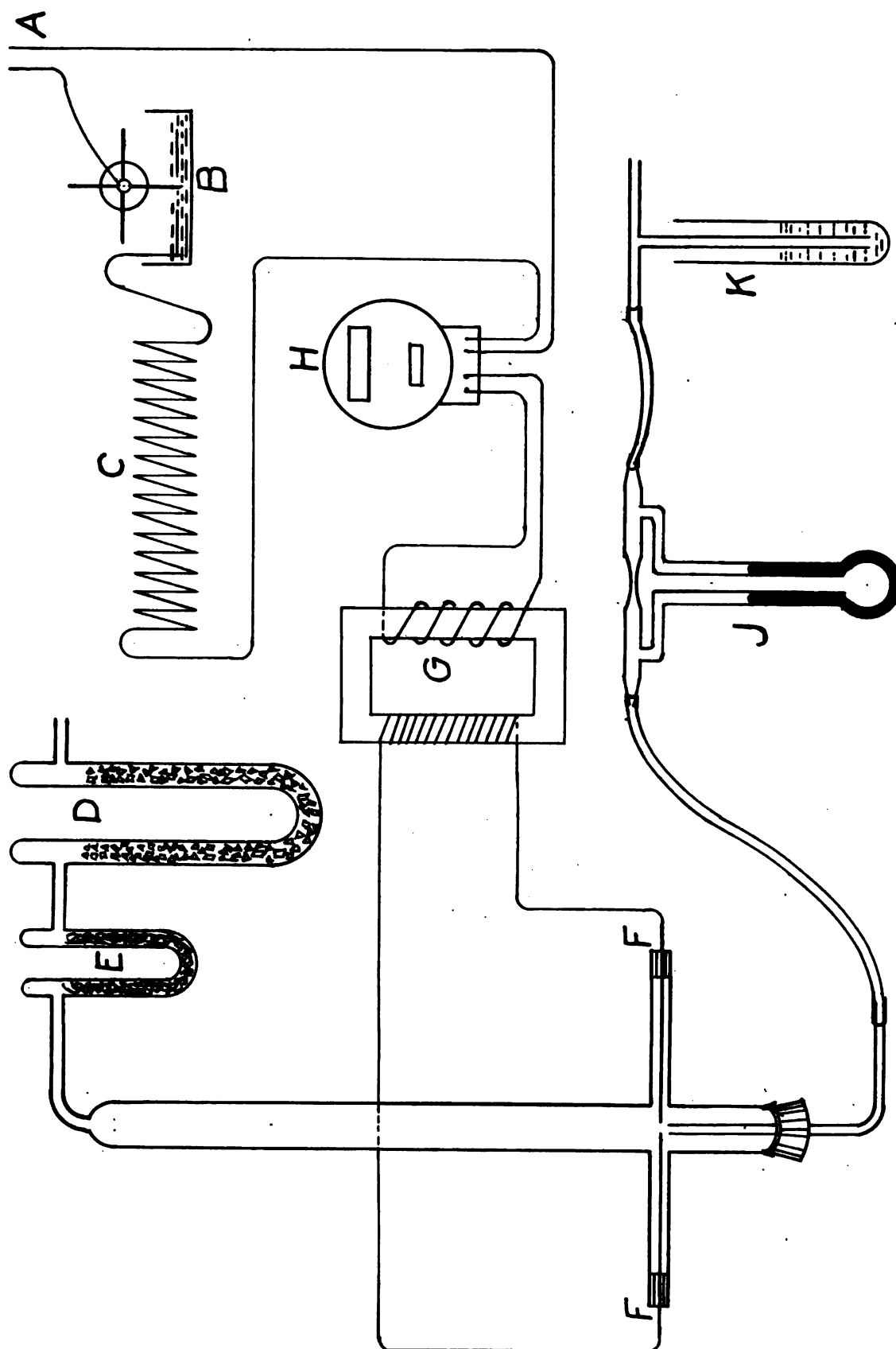
Previous Researches

In past researches along this line high rates of flow have been resorted to in an effort to increase the yield. One difficulty has been the absorption of the oxides. Howles reported that a high rate of flow not only rendered the arc unsteady, but increased the difficulty of absorption. Other investigators have said that the problem of absorption is a difficult

one. In the year 1914 R. Marcus patented a method of making pure silica gel which was suitable for adsorption purposes. In the year 1919 W. A. Patrick patented a cheaper method of making silica gel. Patrick has shown that silica gel could be used to free air from such vapors as water, ether, alcohol, and sulphur dioxide. The adsorption of gases by silica gel is a reversible one, that is, it gives up its adsorbed material at a higher temperature. In order to ascertain whether or not the absorption difficulty could be eliminated by means of silica gel and to study the influence of various factors, it was thought the following research might prove something of interest in the problem of fixation. An attempt was also made to verify some of the conflicting statements which appear in the literature on this subject.

Description of Apparatus

Two ten millimeter pyrex glass tubes twelve inches long were fused to a five centimeter pyrex tube as shown in the drawing. The electrodes were placed inside these two side arms. The connection between the electrodes and the glass was made by means of rubber tubing, since the temperature was not very high at this point. This made it a simple matter to move the electrodes back and forth. The air was supplied from below by means of a five millimeter glass tube at right angles to the electrodes. The end of this glass tube was placed three millimeters from the electrodes and this same glass tube was used throughout the research, so as to eliminate this variable. The air was purified by passing it first through two wash bot-



Explanation of Drawing

A-Line

B-Interrupter

C-Choke coil

D-Silica gel U tube

E-Glass wool tube

F-Electrodes

G-Transformer

H-Meter

J-Flow meter

K-Flow regulator

bles of concentrated sulphuric acid in order to remove a large part of the moisture and all of the oil which is always found in compressed air. The air was then led through two towers which contained potassium hydroxide sticks. The rate of flow was measured by means of a flow meter. This consisted of a small glass nozzle, through which the air was forced, the rate of flow being determined by the difference in the height of oil columns on each side of the nozzle. The flow meter was standardized by connecting it to a bottle out of which water was siphoned. The time required to fill a volumetric flask was determined and at the same time the difference in the oil heights was noted. The time was plotted against the difference in heights and from the curve the rate of flow corresponding to any difference in height could be read off.

The electrodes consisted of one eighth inch steel rods, which were slightly rounded at the ends. The distance between them was adjusted by means of a glass rod of known diameter. The electrodes were moved toward one another until the glass rod just passed between them.

The watt-hour consumption was measured by means of an ordinary service watt-hour meter. The revolutions of the disk for a definite period of time, say one, two, or three minutes, were observed, and knowing the watts per revolution and the length of time which the experiment was allowed to run, the total wattage could be calculated. The constant of the meter used was $\frac{5}{24}$ watt per revolution, thus making it a fairly accurate way of measuring the electrical energy.

The amount of energy delivered to the electrodes was regulated by means of a choke coil. This consisted of an iron core which slipped in and out of a coil of wire, thus increasing or decreasing the reactance. This was found to be a very satisfactory method of regulating the wattage. The choke coil was placed ahead of the meter, so that the energy it used in the form of heat was not measured.

The silica gel was placed in a ten inch U tube, one inch in diameter, and dried by placing it in a bath at about 175°C and passing dry air through until it was constant in weight. The heating was done in order to activate the gel as well as to dry it. The weighed U tube was connected to what might be called the arc chamber by means of Kotinsky cement. The air, before entering the silica gel tube, passed through glass wool so as to remove any electrode particles. Practically all of the nitrogen dioxide was absorbed by the first four inches of silica gel. This could be observed by the brown color. To make sure that all of the oxides were absorbed by means of the gel, a second U tube was connected to the first. The gain in weight of the second U tube was found to be negligible. This was confirmed still further by means of a sodium hydroxide wash bottle. Practically none of the sodium hydroxide was neutralized.

In order to try an intermittent process an interrupter was constructed as follows: four stiff flattened wires were arranged around a wooden hub 90° apart. These were allowed to dip into mercury, and as the hub rotated the circuit was completed

and broken. The wires were placed zigzag around the hub, so that a regular groove would not be made in the surface of the mercury by the rapidly moving wires. Electrical connection was made with the rotating parts by wrapping wire tightly around the shaft on which the hub rotated. The hub made 125 revolutions per minute. This interrupted the arc 500 times per minute, although it looked practically continuous.

In using the interrupter the air flow was such as to sweep the arced air from the electrodes while the arc was out, as the following calculation shows. One liter of air was passed through the five millimeter tube in one minute. The cross section of a five millimeter glass tube is $(3.14)(2.5)^2$ or 19.63 square millimeters. This is equal to .1963 square centimeters. Then a five millimeter tube $\frac{1000}{.1963}$ or 5102 centimeters long has a volume of one liter. The the linear velocity of the gas through the arc is 5102 centimeters per minute. The arc was out $\frac{1}{500}$ of a minute. The gas moved 10.1 centimeters during this interval of time. Since the thickness of the arc was between two and three centimeters, all of the gas must have been removed from the region of the arc while the current was off.

The interrupter was connected ahead of the meter so that the energy it used in arcing at the surface of the mercury was not measured. On a practical basis a permanent interrupter could be constructed to work in an oil bath, thus eliminating any sparking and arcing.

The amperage was determined by means of a hot wire ammeter constructed as follows. A piece of German silver wire was run

through a fifteen millimeter glass tube twelve inches long. A short piece of five millimeter glass tubing was fused to the side of the larger glass tube. This was connected by means of rubber tubing to a U tube which contained paraffin oil. The current in passing through the German silver wire caused it to become heated, thus causing the air to expand. The difference in the height of the oil in the two arms of the U tube was a measure of the current. This was standardized by means of a standard ammeter, storage batteries being used as a source of current, the amount being regulated by means of a resistance coil.

Method of Procedure

In starting an experiment the choke coil was set so that the watt-meter indicated the desired wattage with no air flowing. The current was allowed to run for a short period before the air was turned on in order to avoid any changing conditions. The air was then turned on until the flow meter indicated the desired rate of flow. It was found necessary to readjust the choke coil during the experiment in order to keep the wattage constant. One hour was found to be a convenient length of time in which to let the experiment run, as this caused the silica gel U tube to increase in weight by about one gram. At the end of an experiment the current was shut off, but the air was allowed to flow for a short period in order to sweep all the oxides of nitrogen into the U tube. The U tube was then weighed. Since the number of watts used to produce a certain number of grams of nitrogen dioxide was known, it was a simple

matter to calculate the number of grams per kilowatt hour.

Data

No.	Volts	Amp.	Yield	Electrodes	Flow	Remarks
1	1000	.7	7.6	Iron	.91	Yellow colored arc
2	"	"	4.87	"	.94	"
3	"	"	7.87	"	.90	"
4	"	"	7.47	"	1.00	"
5	"	"	7.47	"	.48	"
6	"	"	5.00	"	Fast	"
7	"	"	8.20	"	Fast	"
8	"	"	5.10	"	Fast	"
9	"	"	4.80	"	1.00	"
10	100		1.47	"	1.00	"
11	100			Carbon	1.00	Gel not colored
12	100			Carbon	1.00	"
13	1000	.7		Carbon	1.00	"
14	20000		1.95	Iron	.95	Spark discharge
15	"		4.80	"	.97	"
16	"		4.92	"	1.00	"
17	"	.2	15.8	"	1.00	White arc
18	"	"	9.00	"	.95	"
19	"	"	12.8	"	1.00	"
20	"	"	14.4	"	1.10	"
21	"	"	3.2	"	Fast	Fuse trouble
22	"	"	16.1	"	1.30	White arc
23	"	"		"	1.00	Impossible result
24	"	"	15.94	"	1.00	Intermittent arc

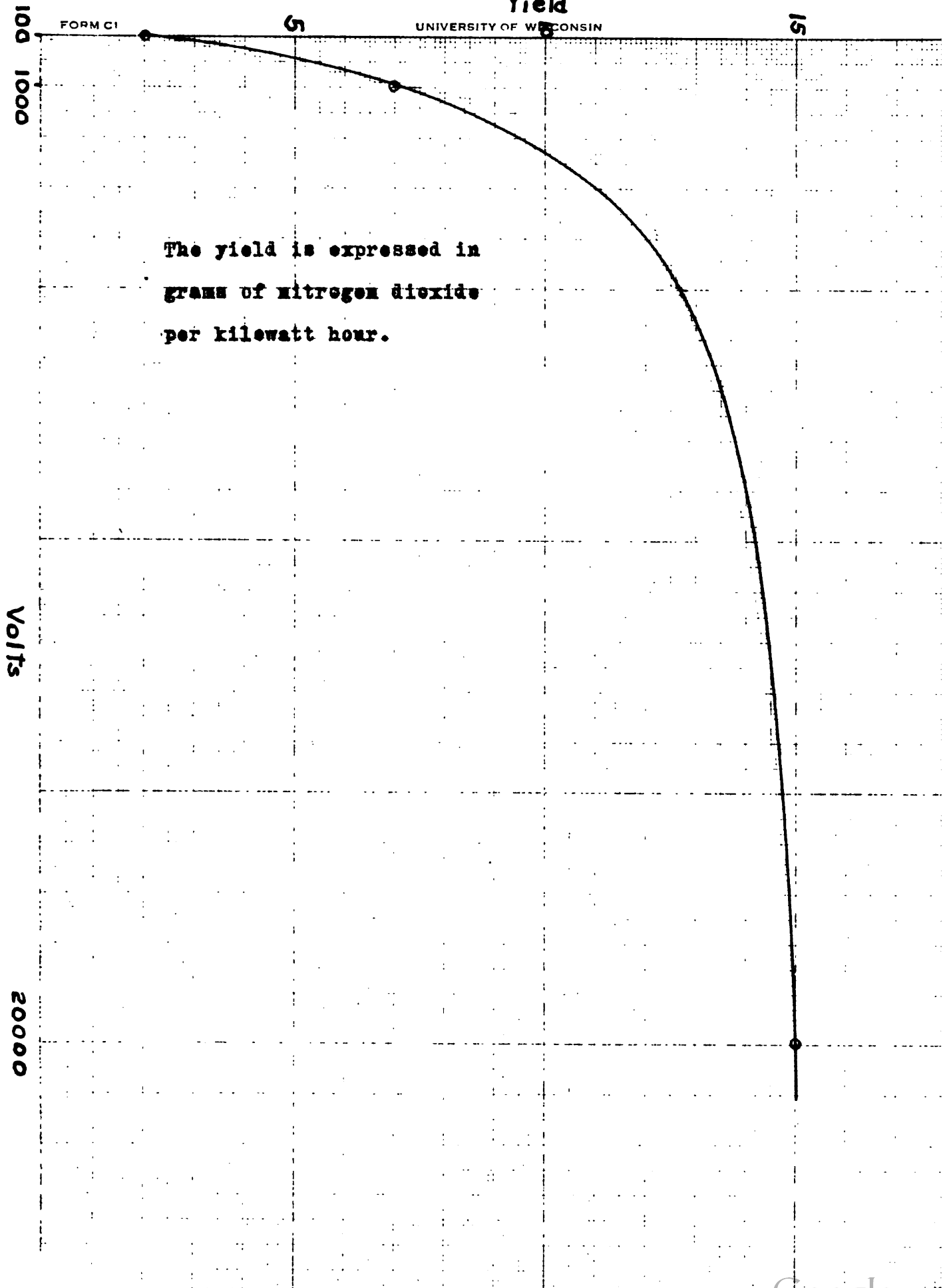
No.	Volts	Amp.	Yield	Electrodes	Flow	Remarks
25	20000	.2	17.4	Iron	.95	Intermittent arc
26	"	"	14.0	"	1.00	"
27	"	"	13.46	"	1.00	"
28	"	"	13.40	"	1.00	"
29	"	"	3.40	"	.95	Moist air
30	"	"	4.60	"	1.20	"
31	"	"	8.36	"	1.00	"
32	"	"	8.86	"	1.00	Small condenser used Blue spark discharge
33	"	"	12.8	"	.95	"
34	"	"	8.12	"	Fast	"
35	"	"	Low	"	1.00	Large condenser used Fat blue spark discharge
36	"	"	Low	"	Very slow	"
37	"	"	4.18	"	1.00	Large condenser, white spark discharge, high wattage
38	"	.2	14.7	"	1.00	White arc, ozonized air used
39	"	"	11.4	"	1.00	"

The small condenser consisted of a Leyden jar. This was connected across the electrodes. The large condenser was a glass plate condenser. This gave a fat blue spark when a moderate amount of wattage was supplied, but when the wattage was increased the spark turned a yellow color. When moist air was used the oxides were absorbed in a sodium hydroxide wash bottle which contained glass beads.

Yield

FORM C1

UNIVERSITY OF WISCONSIN



The yield is expressed in
grams of nitrogen dioxide
per kilowatt hour.

Volts

20000

Discussion of Results

When carbon electrodes were used the gain in weight of the silica gel U tube was considerable, but the gel was not colored brown as it was when the iron electrodes were used. This was undoubtedly due to the fact that the silica gel absorbed large quantities of carbon dioxide and carbon monoxide. The current of air caused the electrodes to burn off very fast. Other investigators have found that carbon electrodes and a low voltage gave a small yield.

From the data it will be observed that the yield increases with the voltage. This indicates that the electrical action enters into the oxidation of nitrogen. The temperature of a 20000 volt arc might be higher than that of a 100 volt arc, but the temperature increase cannot be as great as the increase in the yield indicates it to be if the reaction is a purely thermal one as the following will show. The 20000 volt yield is one thousand percent higher than the 100 volt yield. According to Nernst's data, on page two, the five hundred percent increase in the concentration of nitric oxide is accompanied by a temperature increase of 864° . The increase would be still larger for a thousand percent increase in concentration. From the appearance of the arc and the temperature surrounding, it is hard to see how the temperature increase could even be 864° . If the temperature of the 100 volt arc is less than that of the 20000 volt arc then the thermal decomposition is less. Since the yield of the 100 volt arc is less than that of the 1000 and 20000 volt arc the formation of nitric oxide must have been

less provided a smaller amount has been decomposed. The increase in the yield can be explained by means of the electrical theory by assuming that the greater difference of potential between the electrodes causes more ions to be formed, and that this increase in the number of ions causes the formation of more nitric oxide.

When the condenser was connected across the electrodes the yield was very low. This may be due to the fact that the ultra-violet light causes the decomposition of nitric oxide as it does ozone. A spark discharge without the condenser gives a yield which is below that of the arc. The amount of ultra-violet light in the spark discharge without the condenser is less than when the condenser is used. Since the amount of wattage in both cases is the same it appears that the ultra-violet light has something to do with the difference in yields, although it is possible that the condenser increases the voltage, thus making another variable. The high wattage, indicated in experiment thirty-seven, is 1.5 the ordinary wattage.

Moist air gives a small yield. Other investigators have obtained the same results. This may be due to the fact that some of the energy is used to decompose the water and to raise the temperature of the water vapor to the temperature of the arc. When moist air was used the arc had the same color as when dry air was used.

The interrupted arc gave the same yield as the continuous arc. When the interrupter was used the choke coil was set the same as it was when the continuous arc was used. In other

words, since the current was on half the time and off half the time, if the disk of the meter made six revolutions per minute when the continuous arc was used, then when the interrupted arc was used it made only three revolutions per minute. The grams of nitrogen dioxide produced in a given time was one-half of what was produced by the continuous arc, if the grams per kilowatt hour was the same. Since the current was on only half the time, the average temperature of the arc was probably not as high as it was when the current was continuous. If this is the case, then the thermal decomposition is less.

The rate of flow, between certain limits, exerts an influence on the yield. The fast rate of flow on the data sheet means that the rate of flow is such that the arc is in danger of being blown out. The low yield with a high rate of flow may be due to the fact that the arc is unsteady, or it may be that it is removed from the region of the arc before the electrical or thermal action can take place.

Approved Farrington Daniels.

May 26, 1922.

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